



UNIVERSITI PUTRA MALAYSIA

**MODIFICATION OF MICRO- AND NANO-STRUCTURES OF VANADIUM
OXIDE-BASED CATALYST FOR PARTIAL OXIDATION OF *n*-BUTANE**

WONG YEE CHING

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**MODIFICATION OF MICRO- AND NANO-STRUCTURES OF VANADIUM
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By

WONG YEE CHING

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfilment of the Requirements for the Degree of Doctor of Philosophy**

August 2009



Especially Dedicated To

My Dearest Mum & Dad

**Wong Lee Min
Lim Ho**

My Dear Brother

Wong Yee Seng

My Dear Sister

Wong Yee Chiek

*Without their love and continued support,
this thesis would not have been possible.*

Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in
fulfilment of the requirements for the degree of Doctor of Philosophy

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Chairman: Professor Taufiq Yap Yun Hin, PhD, CChem, FRSC (UK)

Faculty: Science

Sonochemical treatment on V_2O_5 and sonochemical synthesis were employed to produce $VOPO_4 \cdot 2H_2O$ both using ultrasound irradiation. Intercalation-exfoliation-reduction using different mixture of solvent as reducing agent to produce $VOHPO_4 \cdot 0.5H_2O$ and mechanochemical treatment were employed on both $VOPO_4 \cdot 2H_2O$ and $VOHPO_4 \cdot 0.5H_2O$. Besides, the effects of Bi dopant addition also have been studied. The catalysts were synthesised by calcining the precursor, $VOHPO_4 \cdot 0.5H_2O$ in a flow of *n*-butane in air (0.75% *n*-butane in air) for 18 h at 733 K. The physico-chemical properties of the catalysts were characterised by using X-ray diffraction (XRD), BET surface area measurement, redox titration, inductively coupled plasma-atomic emission spectroscopy (ICP-AES), scanning electron microscope (SEM), transmission electron microscope (TEM) and temperature programmed reduction in H_2 flow (H_2 -TPR). The catalytic properties of the selected catalysts were carried out by using temperature programmed reaction (TPRn) and on-line microreactor system. The experimental results indicated that V_2O_5 that undergoes ultrasound irradiation for 30 minutes showed an extremely high *n*-butane conversion (94%) due to its morphology which different from its bulk structures and

with the present of kinetically reactive oxygen species. Moreover, nanostructured VPO catalyst produced using sonochemical treated V_2O_5 for 30 min as starting material also shows drastic increment in *n*-butane conversion (9%) compared to the reference catalyst synthesised via organic route. $VOPO_4 \cdot 2H_2O$ produced through sonochemical synthesis technique drastically reduced the synthesis time to only 15 min compared to the conventional reflux method that consumed the synthesis time up to 24 h. The VPO catalyst produced which undergo sonochemical synthesis for 120 min (VPDS120) shows a drastic increment in *n*-butane conversion (36%) due to its diameters and thickness of platelets which are smaller thus directly increase the active site of the catalyst for oxidation of *n*-butane. Furthermore, VPDS120 catalyst contains more V^{4+} percentage which directly lead to the increment of the total amount of active and mobile oxygen attached to V^{4+} phase (O^- - V^{4+} pair). VPO catalyst produced through intercalation-exfoliation-reduction technique using mixture of 2-butanol and ethanol as reducing agent while doping 1 % bismuth as promoter, IERC(2Bu-Et)RBil gave the highest maleic anhydride (MA) selectivity due to reactive O^{2-} species released from the additional crystalline V^{5+} phase formed (O^{2-} - V^{5+} pair) at relative lower temperature. Mechanochemical treated VPO catalyst, VPDM30 shows both reduction peaks occurred at lower temperature compared to the reference catalyst with a suitable oxygen species ratio from V^{5+}/V^{4+} of around 0.25. The lattice oxygen species in the V^{5+} and V^{4+} phases which are more reactive, mobile and can be removed easily shown to be the main contribution for VPDM30 to gave high *n*-butane conversion. A high amount of active oxygen released from V^{4+} phase (O^- - V^{4+} pair) was shown to be the main contribution for mechanochemical treated bismuth doped VPO catalyst, VPDBiMill to be the most active catalyst for *n*-butane oxidation.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**MODIFIKASI STRUKTUR MIKRO DAN NANO BAGI MANGKIN DASAR
VANADIUM OKSIDA UNTUK PENGOKSIDAAN SEPARA *n*-BUTANA**

Oleh

WONG YEE CHING

Ogos 2009

Pengerusi: Profesor Taufiq Yap Yun Hin, PhD, CChem, FRSC (UK)

Fakulti: Sains

Rawatan sonokimia pada V_2O_5 dan sintesis sonokimia untuk menghasilkan $VOPO_4 \cdot 2H_2O$ dimana kedua-duanya menggunakan pemancaran gelombang ultragema. Interkelasi-exfoliasi-penurunan menggunakan campuran pelarut berbeza sebagai agen penurunan untuk menghasilkan $VOHPO_4 \cdot 0.5H_2O$ dan rawatan mekanokimia juga diaplikasikan pada $VOPO_4 \cdot 2H_2O$ dan $VOHPO_4 \cdot 0.5H_2O$. Selain itu, kesan-kesan dari Bi sebagai dopan juga turut dikaji. Mangkin-mangkin telah disintesis dengan mengkalsinkan prekursor, $VOHPO_4 \cdot 0.5H_2O$ dalam aliran *n*-butana selebihnya udara (0.75 % *n*-butana dalam udara) selama 18 jam pada suhu 733 K. Sifat-sifat fizikal-kimia mangkin telah dicirikan dengan menggunakan pembelauan sinar-X (XRD), pengukuran luas permukaan BET, penitratan redox, plasma gandingan teraruh-spektoskop pancaran atom (ICP-AES), mikroskop elektron imbasan (SEM), mikroskop elektron pemancaran (TEM) dan penurunan suhu terprogram dalam aliran H_2 (H_2 -TPR). Sifat pemangkinan untuk mangkin terpilih telah dijalankan dengan menggunakan tindak balas suhu terprogram (TPR_n) dan sistem rektor mikro on-line. Keputusan-keputusan eksperimen telah menunjukkan bahawa V_2O_5 yang telah mengalami pancaran gelombang ultragema selama 30 min memberi penukaran *n*-butana yang tinggi (94%) disebabkan ia mempunyai morfologi

yang berbeza daripada struktur asalnya dan ia juga memiliki kinetik oksigen spesies yang reaktif. Tambahan pula, struktur nano mangkin VPO yang dihasilkan menggunakan V_2O_5 yang dirawat dengan sonokimia selama 30 min sebagai bahan pemulaan juga menunjukkan peningkatan yang drastik pada penukaran *n*-butana (9%) berbanding dengan mangkin rujukan yang telah disintesis melalui laluan organik. $VOPO_4 \cdot 2H_2O$ yang dihasilkan melalui cara sistesis sonokimia mengurangkan masa sistesis secara mendadak kepada 15 min berbanding dengan cara refluks secara konvensional yang memerlukan masa sebanyak 24 h. Mangkin VPO yang dihasilkan dengan cara sintesis sonokimia selama 120 min (VPDS120) menunjukkan peningkatan penukaran *n*-butana secara mendadak (36%) disebabkan diameter dan ketebalan kepingannya yang kecil yang secara langsungnya meningkatkan tapak aktif mangkin bagi pengoksidaan *n*-butana. Di samping itu, mangkin VPDS120 mempunyai lebih peratus V^{4+} yang secara langsungnya mengakibatkan peningkatan jumlah kuantiti oksigen yang aktif dan bergerak yang terikat dengan fasa V^{4+} (pasangan $O^- - V^{4+}$). Mangkin VPO yang dihasilkan melalui kaedah interkultasi-exfoliasi-penurunan menggunakan campuran 2-butanol dan etanol sebagai agen penurunan disamping didop 1 % bismuth sebagai promoter, IERC(2Bu-Et)RBI1 memberi selektiviti maleik anhidrida yang tertinggi disebabkan spesies O^{2-} yang reaktif yang dibebaskan dari tambahan kristal V^{5+} yang terbentuk (pasangan $O^{2-} - V^{5+}$) pada suhu relatif yang lebih rendah. Mangkin VPO yang dirawat dengan mekanokimia, VPDM30 menunjukkan kedua-dua puncak penurunan wujud pada suhu yang lebih rendah berbanding mangkin rujukan dengan nisbah spesies oksigen dari V^{5+}/V^{4+} yang bersesuaian iaitu sekitar 0.25. Kikisi spesies oksigen dari fasa V^{5+} dan V^{4+} yang lebih reaktif dan mobil mampu dipindahkan dengan lebih senang menjadi sumbangan utama bagi VPDM30 untuk memperoleh penukaran *n*-butana

yang tinggi. Sejumlah oksigen aktif yang tinggi dibebaskan dari fasa V^{4+} (pasangan $O^- - V^{4+}$) menjadi sumbangan utama bagi mangkin VPO yang dirawat dengan mekanokimia dan didop dengan bismuth, VPDBiMill sebagai mangkin yang paling aktif untuk pengoksidaan *n*-butana.

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I certify that a Thesis Examination Committee has met on 25 August 2009 to conduct the final examination of Wong Yee Ching on his thesis entitled "Modification of Micro- and Nano-Structures of Vanadium Oxide-Based Catalyst for Partial Oxidation of *n*-Butane" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the degree of Doctor of Philosophy.


Members of the Thesis Examination Committee were as follows:

Tan Yen Ping, PhD
Lecturer
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Anuar Kassim, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Kamaliah Sirat, PhD
Lecturer
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Mohd. Ambar Yarmo, PhD
Professor
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
(External Examiner)


BUJANG BIN KIM HUAT, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 17 September 2009



This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of Supervisory Committee were as follows:

Taufiq Yap Yun Hin, PhD

Professor

Faculty of Science

Universiti Putra Malaysia

(Chairman)

Mohd. Zobir bin Hussein, PhD

Professor

Faculty of Science

Universiti Putra Malaysia

(Member)


Zulkarnain bin Zainal, PhD

Professor

Faculty of Science

Universiti Putra Malaysia

(Member)


HASANA H. GHAZALI, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 16 October 2009

DECLARATION

I declare that the thesis is my original work except for the quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.



WONG YEE CHING

Date: 4 September 2009

TABLE OF CONTENTS

	Page
DEDICATION	ii
ABSTRACT	iii
ABSTRAK	v
ACKNOWLEDGEMENTS	viii
APPROVAL	ix
DECLARATION	xi
LIST OF TABLES	xvi
LIST OF FIGURES	xviii
LIST OF ABBREVIATIONS	xxi
 CHAPTER	
 1. INTRODUCTION	
1.1 General Introduction to Catalysis	1
1.2 The Importance of Catalysis	2
1.3 Types of Catalysts	3
1.3.1 Homogeneous Catalyst	3
1.3.2 Heterogeneous Catalyst	4
1.4 The Nature of the Catalytic Process	4
1.5 Selective Oxidation	6
1.5.1 Dehydrogenation Reactions	6
1.5.2 Dehydrogenation and Oxygen Insertion Reactions	7
1.5.3 Catalytic Oxidation	8
1.6 The Influence of Nanotechnology Towards Catalysis	11
 2. LITERATURE REVIEW	
2.1 The Production of Maleic Anhydride	15
2.2 Uses of Maleic Anhydride	18
2.3 Worldwide Demand	18
2.4 Process of Oxidising <i>n</i> -Butane	20
2.4.1 The Reaction	20
2.4.2 Catalysts	21
2.5 Vanadyl Pyrophosphate (VO) ₂ P ₂ O ₇	22
2.6 Preparation of Vanadium Phosphorus Oxide Catalyst	23
2.6.1 Method of Preparation of the Precursor	25
2.6.2 Role of P/V Ratio	28
2.6.3 Activation and Conditioning Procedure	29
2.6.4 Role of Promoters	34
2.7 Sonochemically Assisted Synthesis of Vanadium Phosphate Catalysts	42
2.8 Mechanochemical Treatment and Mechanochemically Assisted Synthesis of Vanadium Phosphate Catalysts	45
2.9 Scope and Objectives of This Thesis	49
 3. CATALYSTS SYNTHESIS AND CHARACTERISATIONS	
3.1 Materials and Gases	51

3.2 Synthesis of Bulk Vanadium Phosphorus Oxide Catalysts	52
3.2.1 Organic Route (VPOo)	52
3.2.2 Dihydrate Route (VPD)	53
3.3 Preparation of Nanorod V_2O_5 via Sonochemical Treatment	54
3.4 Preparation of Nanostructured Vanadium Phosphorus Oxide Catalysts using Nanorod V_2O_5 via Organic Method	55
3.5 Modification on $VOPO_4 \cdot 2H_2O$	55
3.5.1 Mechanochemical Treatment	55
3.5.2 Sonochemical Synthesis	56
3.6 Modification on Precursor ($VOHPO_4 \cdot 0.5H_2O$) via Intercalation-Exfoliation-Reduction Technique	57
3.7 Preparation of Bismuth Doped Vanadium Phosphorus Oxide Catalysts	58
3.7.1 Bismuth Metal Dopant	58
3.7.2 Mechanochemical Treatment	59
3.8 Catalysts Characterisations	59
3.8.1 X-Ray Diffraction (XRD) Analysis	59
3.8.2 BET Surface Area Measurements	60
3.8.3 Elemental Analysis	61
3.8.4 Redox Titration	62
3.8.5 Scanning Electron Microscope (SEM)	63
3.8.6 Transmission Electron Microscope (TEM)	64
3.8.7 Temperature Programmed Reduction (TPR in H_2/Ar) Analysis	65
3.8.8 Temperature Programmed Reaction (TPRn in n -Butane/He) Analysis	65
3.9 Catalytic Evaluation	66
 4. PREPARATION AND CHARACTERISATION OF SELF-ASSEMBLED NANOROD V_2O_5 BUNDLES	
4.1 Introduction	69
4.2 Effect of Different Sonochemical Treatment Duration (in minutes) to the Physico-Chemical Properties of Nanorod V_2O_5	70
4.2.1 Phase Identification Using Powder XRD Technique	70
4.2.2 BET Surface Area Measurements and Chemical Analysis	71
4.2.3 Scanning Electron Microscope (SEM)	72
4.2.4 Transmission Electron Microscope (TEM)	74
4.2.5 Temperature Programmed Reduction (TPR in H_2/Ar)	77
4.2.6 Temperature Programmed Reaction (TPRn in n -Butane/Helium)	79
4.2.7 Catalytic Oxidation of n -Butane	81
4.3 Conclusions	84
 5. PREPARATION AND CHARACTERISATION OF NANOSTRUCTURE VANADIUM PHOSPHORUS OXIDE CATALYSTS	
5.1 Introduction	86
5.2 Effect of Different Sonochemical Treatment Duration on Nanorod V_2O_5 as Starting Material to the Physico-Chemical Properties of Nanostructured VPO Catalysts	87

5.2.1 Phase Identification Using Powder XRD Technique	87
5.2.2 BET Surface Area Measurements and Chemical Analysis	88
5.2.3 Scanning Electron Microscope (SEM)	89
5.2.4 Transmission Electron Microscope (TEM)	91
5.2.5 Temperature Programmed Reduction (TPR in H ₂ /Ar)	93
5.2.6 Catalytic Oxidation of <i>n</i> -Butane	96
5.3 Conclusions	98
6. INFLUENCE OF SONOCHEMICAL SYNTHESIS ON VOPO₄·2H₂O AND THE VPO CATALYST PRODUCED	
6.1 Introduction	100
6.2 Effect of Different Sonochemical Synthesis Duration on VOPO ₄ ·2H ₂ O and the Properties of VPO Catalyst	101
6.2.1 Phase Identification Using Powder XRD Technique	101
6.2.2 BET Surface Area Measurements and Chemical Analysis	103
6.2.3 Scanning Electron Microscope (SEM)	104
6.2.4 Transmission Electron Microscope (TEM)	108
6.2.5 Temperature Programmed Reduction (TPR in H ₂ /Ar)	110
6.2.6 Catalytic Oxidation of <i>n</i> -Butane	112
6.3 Conclusions	113
7. INFLUENCE OF INTECALATION-EXFOLIATION-REDUCTION TECHNIQUE TOWARDS THE PHYSICO-CHEMICAL OF VPO CATALYSTS	
7.1 Introduction	115
7.2 Phase Identification Using Powder XRD Technique	116
7.3 BET Surface Area Measurements and Chemical Analysis	119
7.4 Scanning Electron Microscope (SEM)	122
7.5 Transmission Electron Microscope (TEM)	123
7.6 Temperature Programmed Reduction (TPR in H ₂ /Ar)	124
7.7 Catalytic Oxidation of <i>n</i> -Butane	127
7.8 Conclusions	130
8. EFFECT OF MECHANOCHEMICAL TREATMENT ON THE PROPERTIES OF VPO CATALYSTS	
8.1 Introduction	132
8.2 Influence of Different Mechanochemical Treatment Duration on VOPO ₄ ·2H ₂ O and the Properties of VPO Catalysts	133
8.2.1 Phase Identification Using Powder XRD Technique	133
8.2.2 BET Surface Area Measurements and Chemical Analysis	136
8.2.3 Scanning Electron Microscope (SEM)	137
8.2.4 Temperature Programmed Reduction (TPR in H ₂ /Ar)	139
8.2.5 Catalytic Oxidation of <i>n</i> -Butane	142
8.3 Influence of Mechanochemical Treatment on Bismuth Doped VPO Catalysts Precursor	144
8.3.1 Phase Identification Using Powder XRD Technique	144
8.3.2 BET Surface Area Measurements and Chemical Analysis	146
8.3.3 Scanning Electron Microscope (SEM)	148
8.3.4 Temperature Programmed Reduction (TPR in H ₂ /Ar)	150
8.3.5 Catalytic Oxidation of <i>n</i> -Butane	152

8.4 Conclusions	154
9. SUMMARY AND CONCLUDING REMARKS	155
REFERENCES	158
BIODATA OF THE STUDENT	170

LIST OF TABLES

Table		Page
1.1	Phase Combinations for Heterogeneous Catalysis (Bond, 1987)	4
1.2	Essential Catalyst Properties (Twigs, 1989)	5
1.3	Common Oxide-Catalysed Selective Oxidation Reactions (Centi <i>et al.</i> , 2001)	8
2.1	Maleic Anhydride Consumption in the United States for the Year 2000 (Felthouse <i>et al.</i> , 2001)	18
2.2	Total world production and consumption of maleic anhydride (*1000 metric tons) from 1994 until 2004 (Felthouse <i>et al.</i> , 1995)	19
4.1	Total Surface Area and Chemical Analysis for Nanorod and Bulk V ₂ O ₅	71
4.2	Total amount of oxygen atoms removed from nanorod and bulk V ₂ O ₅ by reduction in H ₂ /Ar	78
4.3	Total amount of CO ₂ produced from the nanorod and bulk V ₂ O ₅ by TPRn in <i>n</i> -Butane/Helium	80
4.4	The catalytic performance of self-assembled nanorod and bulk V ₂ O ₅ catalysts synthesised for oxidation of <i>n</i> -butane	81
5.1	Specific BET surface area, chemical properties, average vanadium valence and percentages of V ⁴⁺ and V ⁵⁺ oxidation states present in nanostructured and bulk VPO catalysts	89
5.2	Total amount of oxygen removed from the nanostructured and bulk VPO catalysts by reduction in H ₂ /Ar	95
5.3	The catalytic performance of nanostructured and bulk VPO catalysts synthesised for oxidation of <i>n</i> -butane	96
6.1	Specific BET surface area, chemical properties, average vanadium valence and percentages of V ⁴⁺ and V ⁵⁺ oxidation states present in VPD and VPDS120 catalysts	103
6.2	Total amount of oxygen removed from VPD and VPDS120 catalysts by reduction in H ₂ /Ar	111
6.3	The catalytic performance of sonochemical synthesised VPDS120 and bulk VPD catalysts for oxidation of <i>n</i> -butane	112

7.1	Specific BET surface area, chemical properties, average vanadium valence and percentages of V^{4+} and V^{5+} oxidation states present in IER-VPD catalysts synthesised with different mixture of solvent	120
7.2	Total amount of oxygen removed from the doped and undoped IER-VPD catalysts by reduction in H_2/Ar	126
7.3	The catalytic performance of doped and undoped intercalation-exfoliation-reduction catalysts using different mixture of solvent for oxidation of <i>n</i> -butane	128
8.1	Specific BET surface area, chemical properties, average vanadium valence and percentages of V^{4+} and V^{5+} oxidation states present in mechanochemical treated and untreated catalysts	136
8.2	Total amount of oxygen removed from VPD, VPDM30 and VPDM60 catalysts by reduction in H_2/Ar	141
8.3	The catalytic performance of mechanochemical treated and untreated VPO catalysts for oxidation of <i>n</i> -butane	142
8.4	Specific BET surface area, chemical properties, average vanadium valence and percentages of V^{4+} and V^{5+} oxidation states present in mechanochemical treated and untreated bismuth doped catalysts	147
8.5	Total amount of oxygen removed from mechanochemical treated and untreated bismuth doped VPO catalysts by reduction in H_2/Ar	151
8.6	The catalytic performance of bismuth doped mechanochemical treated and untreated VPO catalysts for oxidation of <i>n</i> -butane	152

LIST OF FIGURES

Figure		Page
2.1	Schematic representation of the idealised structure of $(VO)_2P_2O_7$ (Cavani <i>et al.</i> , 1985)	23
2.2	Transformation of precursor to the active phase (Cavani and Trifirò, 1994)	31
3.1	Schematic diagram of the plug flow reactor	67
4.1	XRD patterns of sonochemical treated (S30-S240) and untreated V_2O_5	70
4.2	SEM micrographs of V_2O_5 (a) S30, (b) S60, (c) S90, (d) S120, (e) S180 and (f) S240 (with 15000 \times magnification)	73
4.3	TEM micrograph of untreated bulk V_2O_5	74
4.4	TEM micrographs of (a) S30, (b) S60, (c) S90, (d) S120, (e) S180 and (f) S240	75
4.5	TPR profiles for sonochemical treated and untreated V_2O_5	77
4.6	TPRn of <i>n</i> -Butane/Helium stream over synthesised V_2O_5	80
4.7	<i>n</i> -Butane conversion as a function of the duration of sonochemical treatment	83
4.8	<i>n</i> -Butane conversion as a function of percentage of V^{5+}	83
5.1	XRD patterns for nanostructured and bulk VPO catalysts	88
5.2	SEM micrographs of (a) VPO (5000 \times), (b) SRVPO30, (c) SRVPO60, (d) SRVPO90, (e) SRVPO120 and (f) SRVPO180 (with 10000 \times magnification)	90
5.3	TEM micrographs of (a) VPO, (b) SRVPO30, (c) SRVPO60, (d) SRVPO90, (e) SRVPO120 and (f) SRVPO180	92
5.4	TPR profiles for the nanostructured and bulk VPO catalysts	94
5.5	The catalytic performance of the nanostructured and bulk VPO catalysts as a function of the duration of sonochemical treatment	97
6.1	XRD patterns of sonochemical synthesised vanadyl phosphate dehydrate (DS15-DS120)	102
6.2	XRD patterns of VPDS120 and VPD catalyst synthesised	103

6.3	SEM micrograph of VOPO ₄ (with 5000× magnification)	105
6.4	SEM micrograph of (a) DS15, (b) DS30, (c) DS45, (d) DS60, (e) DS90 and (f) DS120 (with 10000× magnification)	106
6.5	SEM micrograph of VPD (with 5000× magnification)	107
6.6	SEM micrograph of VPDS120 (with 5000× magnification)	108
6.7	TEM micrograph of (a) DS15, (b) DS30, (c) DS45, (d) DS60, (e) DS90 and (f) DS120	109
6.8	TPR profiles for VPD and VPDS120 catalysts	111
7.1	XRD patterns for IER-VPD precursors	117
7.2	XRD patterns for IER-VPD catalysts	118
7.3	SEM micrographs of (a) IERC(2Bu-Et), (b) IERC(2Bu-Et)RBi1, (c) IERC(isoBu-Et) and (d) IERC(isoBu) (with 15000× magnification)	122
7.4	TEM micrographs of (a) IERC(2Bu-Et), (b) IERC(2Bu-Et)RBi1, (c) IERC(isoBu-Et) and (d) IERC(isoBu)	124
7.5	TPR profiles for the IER-VPD catalysts	125
7.6	The relation between conversion (%), MA selectivity (%) and MA yield (%) of catalysts produced in <i>n</i> -butane oxidation	129
8.1	XRD patterns of mechanochemical treated (DM30-DM60) and untreated vanadyl phosphate dehydrate (VOPO ₄)	134
8.2	XRD patterns of mechanochemical treated (VPDM30-VPDM60) and untreated VPO catalysts (VPD)	135
8.3	SEM micrograph of VPD (with 5000× magnification)	138
8.4	SEM micrograph of VPDM30 (with 5000× magnification)	138
8.5	SEM micrograph of VPDM60 (with 5000× magnification)	139
8.6	TPR profiles for VPD, VPDM30 and VPDM60 catalysts	140
8.7	The catalytic performance of the synthesised VPO catalysts as a function of the duration of mechanochemical treatment	143
8.8	XRD patterns for mechanochemical treated and untreated bismuth doped vanadyl phosphate hemihydrate	144

8.9	XRD patterns for mechanochemical treated and untreated bismuth doped VPO catalysts	146
8.10	SEM micrograph of VPDBi (with 10000× magnification)	149
8.11	SEM micrograph of VPDBiM60 (with 10000× magnification)	149
8.12	TPR profiles for mechanochemical treated and untreated bismuth doped VPO catalysts	150
8.13	MA selectivity as a function of <i>n</i> -butane conversion	153

LIST OF ABBRIVIATIONS

BET	Brunauer Emmer Teller
FWHM	Full-Width at Half Maximum
GHSV	Glass Hourly Space Velocity
H ₂ -TPR	Temperature Programmed Reduction in Hydrogen
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
JCPDS	Joint Committee on Powder Diffraction Standard
MA	Maleic Anhydride
MS	Mass Spectrometer
m/z	Mass to charge ratio
P/V	Phosphorus/Vanadium
rpm	Round per minute
SEM	Scanning Electron Microscope
T _{max}	Temperature at peak maximum
TEM	Transmission Electron Microscope
TCD	Thermal Conductivity Detector
TPR _n	Temperature Programmed Reaction
VPO	Vanadium Phosphorus Oxide
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 General Introduction to Catalysis

Berzelius in 1836 introduced the term ‘catalysis’ (Bond, 1987), where he derived it from the Greek words *kata*, which stands for down and *lysein*, which means to split or break. Later in 1895, Ostwald was the first to write down a definition of a catalyst: “A catalyst is a substance that changes the rate of a chemical reaction without itself appearing in the products”. So, it is important to note that a catalyst does not influence the thermodynamic equilibrium of reactants and products. Therefore, the current definition is slightly better, though close to Ostwald’s description: “A catalyst is a substance that increases the rate of approach to thermodynamic equilibrium of a chemical reaction without being substantially consumed”. Catalysis is the phenomenon of a catalyst in action (Gates, 1992).

As befits a committee a longer, although more precise, description has been suggested by the UK Science Research Council (Hartley, 1985): A system is said to be “catalyzed” when the rate of change from state I to state II, is increased by contact with a specific material agent which is not a component of the system in either state and when the magnitude of the effect is such as to correspond to one or more of the following descriptions:



- (i) Essentially, measurable change from state I to state II occurs only in the presence of the agent.
- (ii) A similarly enhanced rate of change is found with the same sample of agent in repeated experiments using fresh reactants.
- (iii) The quantity of matter changed is many times greater than that of the agent.

1.2 The Importance of Catalysis

Catalysts are among the most important technological materials, being used in the manufacture of chemicals, fuels, foods, clothing, pharmaceuticals, and materials such as organic polymers (Gates, 1992). The value of the goods manufactured in the United States in processes that at some stage involve catalysis is about \$1 trillion annually; the catalysts used in these processes cost only a few tenths of a percent of the value of the products.

Today, almost 70% of all chemicals that are produced have been in contact with a catalyst somewhere in their synthesis process (Matthijs, 1999). This number stresses the importance of the role of catalysis in the chemical industry. Without a catalyst, processes are less clean and sometimes impossible to perform. In principal, catalysis can be used to abate environmental pollution in two ways:

- (i) for cleaning of outgoing waste gases or water (end-of-pipe catalysis),

- (ii) for improvement or replacement of existing processes in such a way that less harmful waste is produced (process-incorporated catalysis).

With regard to (i), two well known examples are the three-way catalyst, which is used to reduce the levels of CO, NO_x and VOC's in automotive exhaust gases, and the Claus catalyst utilised to convert sulphur (H₂S) from industrial exhaust gases.

The subject of this report is closely related to catalysis of type (ii), *i.e.* improvement of an existing process to achieve a higher product yield, and thus fewer byproducts. It is an important for the production of bulk and fine chemicals as well as minimise trace pollutants and contaminants (Hodnett, 2000).

1.3 Types of Catalysts

Generally, catalytic reactions can be divided into two major types, such as homogeneous and heterogeneous (Thomas and Thomas, 1997).

1.3.1 Homogeneous Catalyst

When the catalyst is of the same phase as the reactants and no phase boundary exists, we speak of homogeneous catalysis. This may take place either (Bond, 1987):

- (i) In the gas phase, as, for example, when nitrogen oxide catalyses the oxidation of sulphur dioxide; or